Temperature behaviour of $REAlO_3$ (RE=Nd, Sm, Ho, Tm) crystal structures

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Rare-earth (RE) perovskite-type aluminates $REAlO_3$ and their solid solutions prove oneself as promising materials for laser optics, substrate materials, scintillators and dielectrics. The literatue data on the precise investigations of the thermal behaviour of the structures of this compounds are limited. Last year we reported the high–temperature behaviour of several $REAlO_3$ compounds (RE=Eu, Gd, Tb, Dy, Y, Er, Yb, Lu). In the present communication we report the results of the low– and high-temperature investigations of $NdAlO_3$, $SmAlO_3$, $HoAlO_3$ and $TmAlO_3$.

All high-temperature structural experiments were performed in a STOE capillary furnace at the powder diffractometer at beamline B2, whereas at low-temperature measurements the Oxford Cryosystem closed cycle helium cryostat has been used. The wavelength was determined using 6 reflections of Si (NBS640b standard). Full patterns were collected in the Debye-Scherrer geometry using the on-site readable image plate detector OBI and 0.3 mm capillaries. Analysis of the data was carried out by the Rietveld method using the WinCSD program package.

Following Howard et al. [1], $NdAlO_3$ posesses a rhombohedral structure in the temperature range 295 – 1673 K. Our low-temperature structural investigation proved that $NdAlO_3$ remains rhombohedral at least down to 12 K. Low- and high-temperature investigations of $SmAlO_3$ performed in the temperature range 12 – 1223 K confirmed the presence of a *Pbnm* – *R*-3*c* phase transition between 1023 and 1073 K, which is in a good agreement with the literature data [2] (1058 K). The results of the Rietveld refinement for $SmAlO_3$ are presented in Fig. 1. The $HoAlO_3$ and $TmAlO_3$ structures have been found to be orthorhombic in the temperature range 298 – 1173 K.

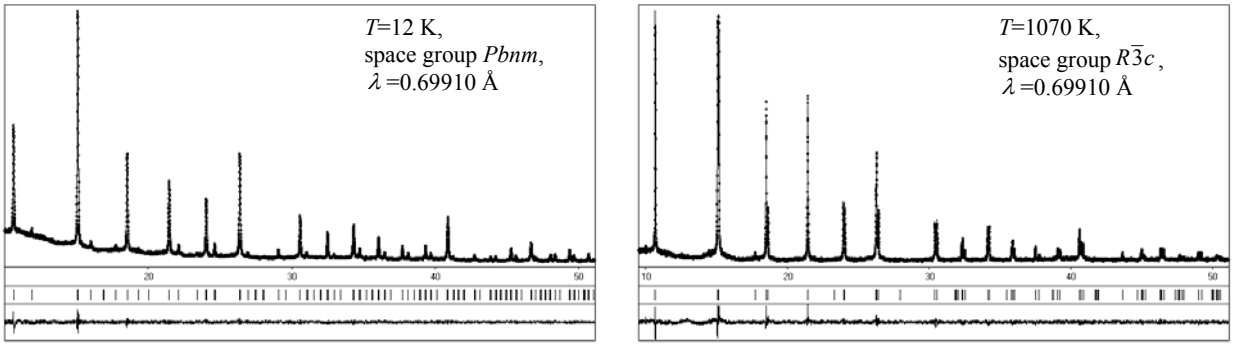

Figure 1: Results of the Rietveld refinement of $SmAlO_3$ at 12 K (a) and 1070 K (b) measured using the image plate detector OBI.

Thermal dependencies of the perovskite-like lattice parameters of the structures investigated are presented in Fig. 2a,b. The parameters of the perovskite cell a_p, c_p and $\Delta\phi$ are derived from the orthorhombic (a_{or}, b_{or}, c_{or}) and rhombohedral (a_{rh}, c_{rh}) cell parameters according to the following relations:

$$a_p = \frac{\sqrt{a_{or}^2 + b_{or}^2}}{2},\ c_p = \frac{c_{or}}{2} \text{ and } \beta_{pr} = 2\arctan\left(\frac{b_{or}}{a_{or}}\right),$$

$$a_p = \frac{\sqrt{12a_{rh}^2 + c_{rh}^2}}{6} \quad \beta_{po} = \arccos\left(1 - \frac{a_{rh}^2}{2a_p^2}\right) \text{ and } \Delta\phi = \pi/2 - \beta$$

where the angle $\Delta\phi$ stands for the measure of monoclinity degree of the perovskite lattice and has a physical meaning of anisotropy between *a* and *b* lattice parameters in orthorhombic structures or *a* and *c* in rhombohedral perovskites**.**

High-temperature lattice parameters of $NdAlO_3$ are taken from Ref. [1]. These data are in good agreement with the LT parameters, obtained in our experiments. The observed lattice parameters (Fig. 2a) increase nonlinearly and monotonically with temperature. Only for the case of $SmGaO_3$ a jump of the lattice parameters associated with the structural phase transition, has been observed. The angle of monoclinity $\Delta\phi$ shows a very interesting behaviour: for the orhthorhombic structures the thermal dependencies of the angle $\Delta\phi$ show a decreasing behaviour with increasing temperature, whereas for the case of rhomboedral structure at increased temperatures $\Delta\phi$ increases also. We associated this feature to the change of the tilting system (e.g. in Glazer's notation) in octahedral framework.

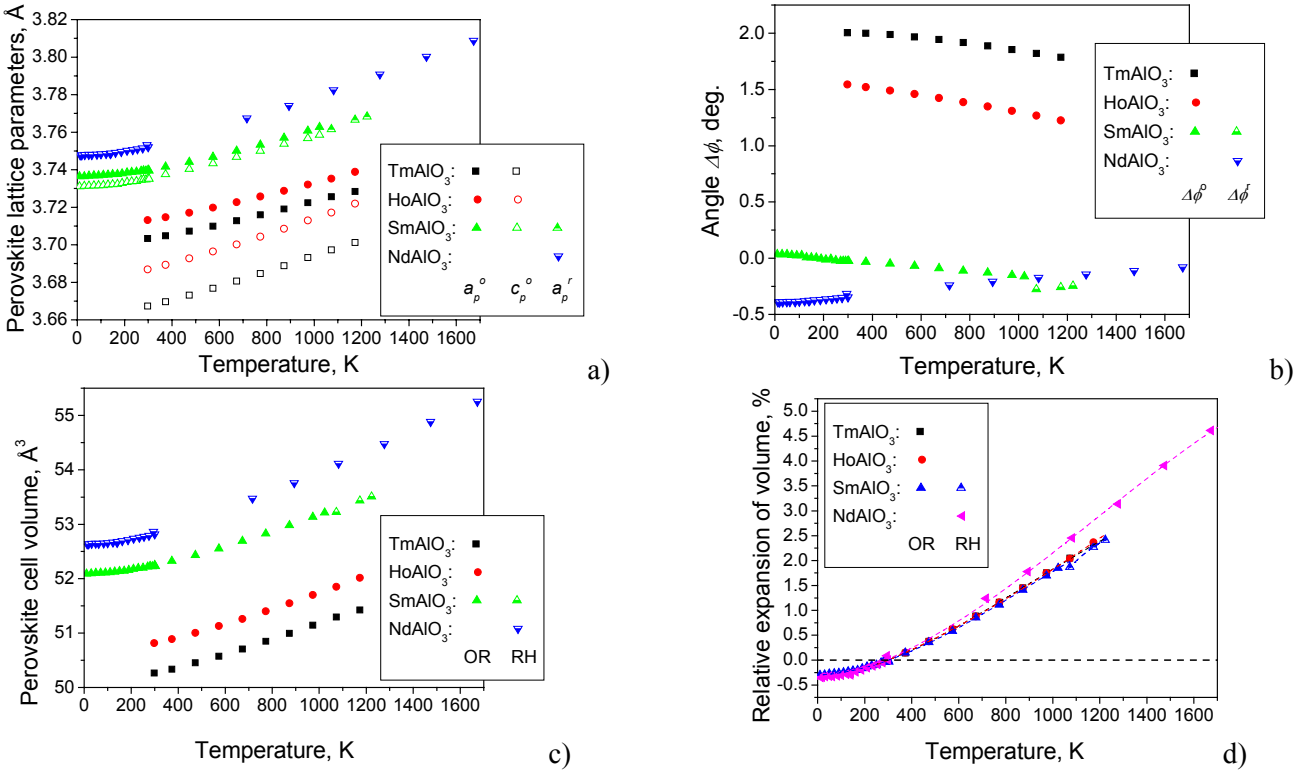

Figure 2: Thermal dependencies of the perovskite cell parameters

The largest values of angles of monoclinity $\Delta\phi$ were observed for the thullium and holmium orthoaluminates due to the relatively low Goldschmidt tolerance-factors. The $\Delta\phi$ angle for $SmAlO_3$ was observed to be very close to zero, which indicates a pseudotetragonality of the perovskite cell, but the character of the octahedral tilts confirms an orthorhombic structure.

The thermal expansion was observed to be higher in the case of rhombohedral structures ($NdAlO_3$ and high-temperature $SmAlO_3$) compared to orthorhombic structures. This is confirmed by analyzing the relative thermal expansion of the cell volume (Fig. 1d), calculated according to the expression $dV(T) = (V(T) - V(T_0))/V(T_0) \times 100\%$, where $V(T_0)$ is the corresponding cell volume at $T = 298$ K.

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References

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